DISTRIBUTION OF *N*-ALKANES IN SURFACE SOILS OF KUANTAN CITY, PAHANG, MALAYSIA

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ABSTRACT

A study has been carried out to determine the distribution of aliphatic hydrocarbons in surface soils of Kuantan City, Pahang, Malaysia. Thirty soil samples (0-15cm depth) were collected from area around Kuantan City covering town center, schools, recreation areas and industrial zones. Hydrocarbons were extracted with dichloromethane using ultrasonic agitation technique and fractioned with silica-alumina column. Characterization of individual hydrocarbon components was carried out using Gas Chromatography – Flame Ionization Detector (GC-FID). Total identified resolved aliphatic hydrocarbon (TIRAH) concentrations in soil samples were found ranging from 0.37 to 139µgg^{-1}. Carbon preference index (CPI) values for higher plant wax *n*-alkanes varied between 0.39 and 1.40, with a mean value of 1.11. No significant correlation between soil organic matter content and the concentrations of *n*-alkanes was observed. Results indicated that the aliphatic hydrocarbons were from both biogenic and anthropogenic sources.

KEYWORDS: Aliphatic Hydrocarbons, Soil

INTRODUCTION

Soils have been considered as the final sink for organic compounds derived from various sources such as natural terrestrial plant wax, urban and industrial emissions, and smoke from biomass burning [1]. The organic compounds in soils comprise fatty acids, sterols, *n*-alkanes, *n*-alkanols and the aromatics, as well as some pesticides and herbicides from agricultural activities. Among all, *n*-alkanes and polycyclic aromatic hydrocarbons (PAHs) have been studied extensively to monitor pollution due to increased utilization of fossil fuels. Characterization of *n*-alkanes based on the related diagnostic parameters [2-3], reflects their origin from biogenic and/or anthropogenic sources. Recently, several reports have been published on the *n*-alkanes and PAHs contamination in Malaysia including Prai Strait, Penang [4], Setiu Wetland, Terengganu [5] and Langat River [6]. However this type of study is still limited particularly in the state of Pahang.

Kuantan (3°49'0"N 102°20'0"E), the state capital of Pahang, is one of the rapid growing cities in east coast of Peninsular Malaysia, located 250km away from the federal capital of Kuala Lumpur. The National Physical Plan 2005 identified Kuantan as one of the future growth centres and a hub for trade, commerce, transportation and tourism due to its favourable geographical position. The characterization of *n*-alkanes in Kuantan soil are, therefore, important in terms of pollution control, risk management and establish a background level of hydrocarbons in soils of this area. The main objective of this study is to provide some baseline data on the degree of pollution by hydrocarbons in the study area.

MATERIALS AND METHODS

Surface soil samples (5cm from the ground surface) (n=30) were collected using metal spade from various location (Figure 1). The roots and grass part were removed and sub-samples were pooled together and wrapped with aluminium foil. Soil samples were then dried using Laminar-flow technique and sieved through a 200µm sieve. Sieved samples were put into clean specimen bottle and labeled accordingly before further analyses were carried out.

TOC (total organic carbon) in soils were analysed using Walkey's and Black titration method, in which the organic carbon is oxidized by dichromate ions, and the quantity of excess dichromate ions is then back titrated with ferrous ion. The procedures for the extraction and fractionation of aliphatic hydrocarbons were adopted from Mohd Tahir et al. [7]. Briefly, 10g of soil samples were extracted three times using ultrasonic agitation for a 30-min period with 50mL of dichloromethane. Alumina-silica column was used for the fractionation of the extract. Predeuterated *n*-tetracosane (n-$C_{24}D_{50}$) was added to the soil prior to extraction as internal standard.

Identification and quantification of *n*-alkanes were carried out by using Agilent Technologies 7890A GC system equipped with a flame ionization detector (FID) and HP-5 capillary column (30 m x 0.32mm). The carrier gas was nitrogen, while oven was programmed from 50^{o}C (held for 1 min) initially to 140^{o}C at a rate of 5^{o}C/min and slowed down to 3^{o}C/min to 290^{o}C (held for 17 min).

For quality assurance and quality control, the laboratory blank and spiked matrix (internal standard spiked into soil) was analyzed. Results showed that there were no significant background interferences. The mean recovery of the multi-step procedure for n-$C_{24}D_{50}$ was 1.09±0.19. Statistical analysis showed that the mean recovery was not significantly different from 1.00 (t<2), therefore no correction has been made for the reported concentration of *n*-alkanes in this study. The detection limits of the method range from 0.31-2.25µgg^{-1}. All concentrations were expressed on a soil dry weight basis.

RESULTS

Surface soils in the study area contained relatively low organic carbon, with value ranging from 0.36% to 4.48%. Weak correlation between %OC and Total Identified Resolved Aliphatic Hydrocarbon (TIRAH) (*r* value = 0.17) suggested that TOC did not play a role in controlling the distribution of hydrocarbons in this study area. The concentrations, diagnostic indices of aliphatic hydrocarbons were presented in Table 1. The *n*-alkanes identified in the soil samples were ranged from n-C_{17} to n-C_{36} with TIRAH concentration ranging from 0.40µg/g to 139µg/g. Comparison with other similar study showed that the TIRAH concentrations observed in this study were relatively higher than those reported in soils collected from Beijing outskirts [8]. The odd numbered carbon compounds in the range of n-C_{25} to n-C_{33} are strongly predominated and most samples exhibit C_{max} at n-$C_{27,}$ n-C_{29}, n-C_{31} and n-C_{33}, in which the distribution indicates a terrigenous input from higher plant waxes [3].

Carbon Preference Index (CPI) has been a useful parameter for estimating biogenic or anthropogenic contributions of aliphatic hydrocarbons. $CPI_{(C24-C34)}$ values for all stations were in the range of 0.39-1.40 (mean = 1.12). The contour map of CPI in soil samples were showed in Figure 2. Lowest value of CPI was found at the northeast site of the city (Indera Makhota, a satellite town developed since 1983), indicating significant contribution of fossil fuel (possibly through deposition of engine oil and industrial activities) besides terrestrial plant epicuticular waxes in the area. CPI values closed to 1 were found at the inner city and the value increased with increasing distance to the city center. This indicated a larger proportion of vascular plant *n*-alkanes in these areas [9].

The terrestrial higher plant wax n-alkane signature was calculate as follows: Wax n-C_n = $[C_n]$ -0.5$[C_{(n+1)}+C_{(n-1)}]$, where negative values of C_n were taken as zero [2]. Results showed significant contribution of biogenic wax *n*-alkane in these stations, with value ranging from 4.15% to 14.8% WNA. However, the wax composition was lower than that reported by Zhu et al. [8].

Generally, the presence of unresolved complex mixture (UCM) in the chromatogram is taken as indicator of petroleum input or bacteria source [2]. C_{max} at n-$C_{27,}$ n-C_{29}, n-C_{31} and n-C_{33}, CPI>1 and the absence of UCM in all chromatograms strongly indicated a predominance of biogenic hydrocarbon inputs to Kuantan surface soil rather than petrogenic hydrocarbons input.

CONCLUSIONS AND DISCUSSION

The concentration of total identified resolved aliphatic hydrocarbons (TIRAH) in Kuantan soils ranged from 0.37 to 139µgg^{-1}. Higher total concentration of aliphatic hydrocarbons was clustered at the southeast sites of the city. Based on the distribution patterns and diagnostic indices, it can be concluded that *n*-alkanes in soils from Kuantan city were mainly from biogenic sources with minor contribution of anthropogenic sources.

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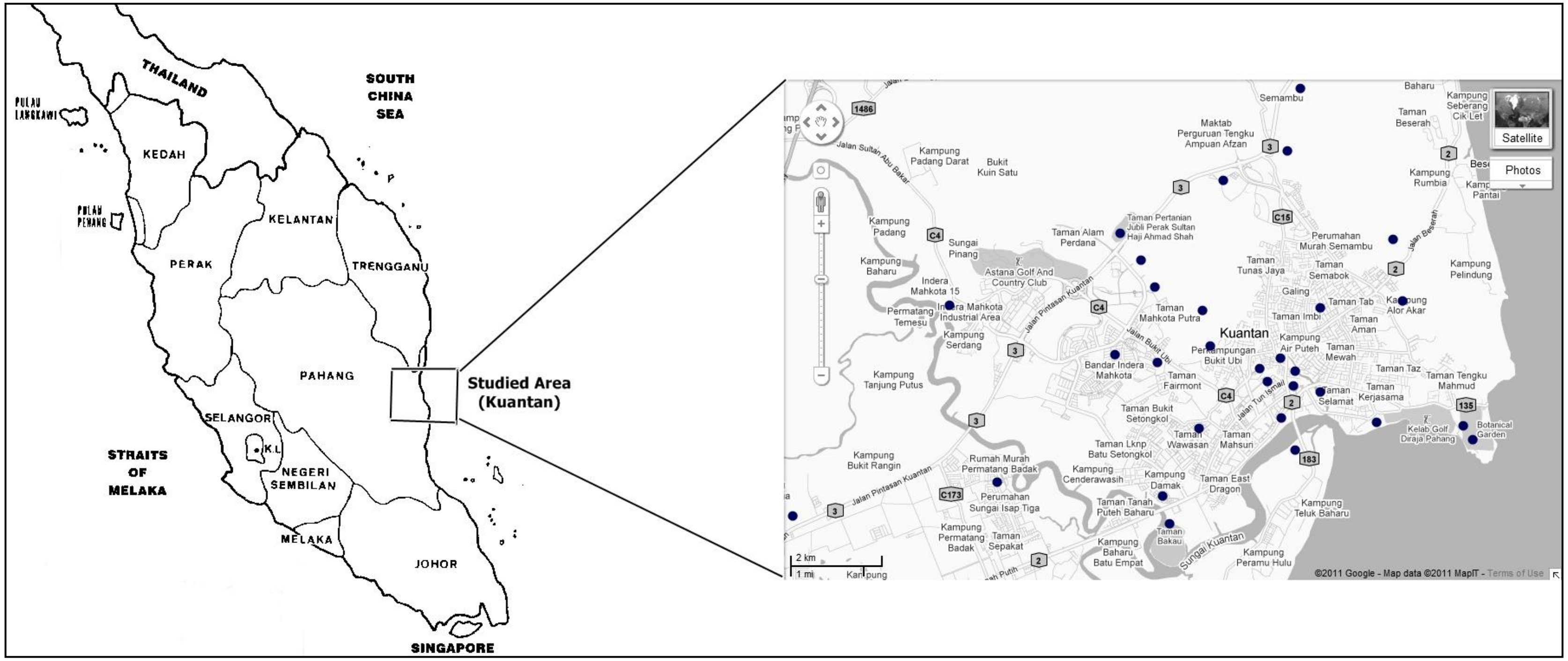

Figure 1: A map showing the sampling locations.

Table 1: Concentrations and diagnostic indices of aliphatic hydrocarbons in soil samples.

Compound	Minimum	Maximum	Median	SD (n=30)
C17	n.d.	0.02	-	0.00
C18	n.d.	n.d.	-	-
C19	n.d.	n.d.	-	-
C20	n.d.	n.d.	-	-
C21	n.d.	n.d.	-	-
C22	n.d.	0.36	0.00	0.09
C23	n.d.	1.21	0.33	0.30
C24	n.d.	3.70	0.95	0.76
C25	n.d.	8.57	2.28	1.76
C26	n.d.	13.5	3.55	2.71
C27	0.03	17.9	4.66	3.72
C28	0.05	17.9	4.65	3.73
C29	n.d.	18.5	4.80	3.97
C30	0.01	15.3	3.93	3.17
C31	n.d.	14.0	3.62	3.06
C32	0.19	9.35	2.24	1.83
C33	n.d.	6.95	1.93	1.71
C34	n.d.	5.02	1.17	0.99
C35	n.d.	4.47	1.32	1.08
C36	n.d.	2.32	0.00	0.61
TIRAH (µg/g)	0.37	139	35.5	28.7
CPI (C_{24}-C_{34})	0.39	1.40	1.12	0.16
% OC	0.36	4.48	1.49	0.88
% of WAN	4.14	14.8	5.71	2.46
% of terrestrial	26.7	49.2	42.8	4.13

n.d.: not detected; -: data not available

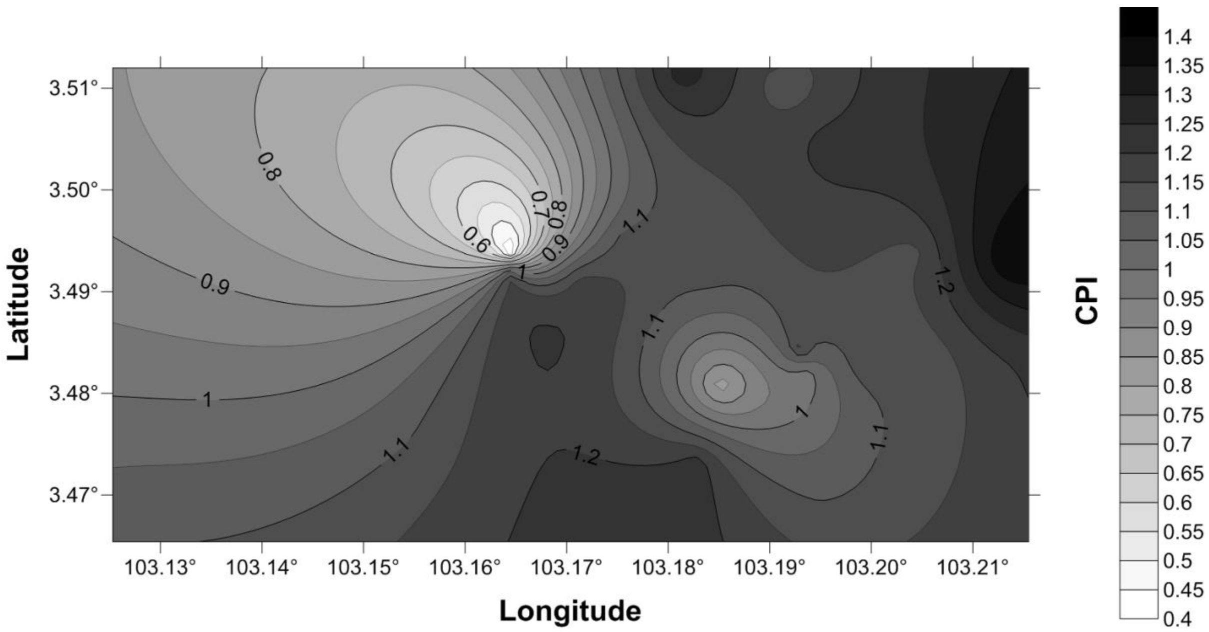

Figure 2: The contour map of CPI $_{(C24-C34)}$ in soil samples.